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Inhibitory Effect of Extracts of *Amella radican* on Corrosion of Carbon Steel Sheets in HCl Solution

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Abstract: The measurement of the corrosion inhibiting capacity of the extracts of *Acmella radicans* was carried out in Hydrochloric acid (HCl) on carbon steel sheets. In the first instance an extraction was conducted in aqueous medium with the Soxhlet equipment. Subsequently, a phytochemical characterization is performed to identify the presence of chemical compounds with anticorrosive potential. It was evidenced the presence of coumarins, flavonoids and tannins. The latter by its OH-group around the aromatic rings, like the carbonyl groups can interact with the cations on the surface of the adsorbed metal which protects it. The tannins were those with the main concentration 2.82 g/L while saponins and triterpenes had practically no presence in this extract and the flavonoids and coumarins had a lower concentration than tannins 0.94 and 0.06 g/L, respectively. The anti-corrosion capacity was measured by weight loss tests and Linear Scanning Voltamperometry (LSV) where 1 Molar (M) solutions of HCl were prepared with inhibitor concentrations based on extracts of Acmella ranging from 2400, 4800 and 7200 parts per million (ppm). The concentrations of 4800 and 7200 ppm were found to have the highest efficacy inhibitor with values above 80%. The Linear Sweep Voltamperometry (LSV) test reveals the mixed character of the inhibitor and a change in the cathodic of the branch.

Key words: Inhibitor, corrosion, carbon steel, extracts, *Acmella radicans*, electrochemistry

INTRODUCTION

Corrosion refers to the deterioration of a material due to the interaction it makes with the environment. This is a destructive process as a result of a chemical attack caused by the environment. Corrosion is a problem with a high negative impact on society as the deterioration of equipment and pipes for example can result in millionaire losses in the industrial processes and can also lead to serious human and economic losses of between 2 and 4% of Gross Domestic Product (GDP) in industrialized countries (Huynh, 2004). Inhibitors have been implemented for the phenomenon of corrosion which are chemicalsthat added in small concentrations in the environment to reduce the rate of corrosion. These are used in two different ways as a contingent measure or as pre-treatment in new structures or freshly cleaned (Ehteram, 2008; Touafri *et al*., 2008; Chitra and Anand, 2016).

Inhibitors are generally of two types; passivator type which are inorganic species (such as chromates, nitrites, molybdates, etc.) that react electrochemically with the metal phase to be protected and those of the filmic type (contain organic substances) whose anti-corrosive activity has been proven by weight loss and electrochemical tests and have proved to be highly efficient for use in the industry. Among these organic substances are *Azadirachta indica* (Neem) *Punica granatum* (pomegranate) and *Momordica charantia* (natural honey) (Quraishi *et al*., 1999; El-Etre and Abdallah, 2000; Orubite and Oforka, 2004).

The purpose of this project is to evaluate the efficiency of the extracts of *Acmella radicans* (Var. Radicans) in the inhibition of corrosion of carbon steel in acid medium for which a characterization of these extracts was carried out by phytochemical tests to find the presence of coumarins, flavonoids tanins, cumarins, saponins and triterpenes due to the presence of heteroatoms in their structures that give them anticorrosive properties (Bhawsar *et al*., 2015). The results of the experiments were carried out in order to calculate the corrosion rate and with it the inhibitory efficiency of each of them.

The experiments were carried out as follows; extraction of the inhibitor of the *Acmella radicans* plant

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using the Soxhlet equipment, extract characterization, weight loss tests and Linear Scanning Voltammetry (LSV). This project seeks to expand the field of green corrosion inhibitors, allowing the incorporation of an easily obtainable inhibitor that presents high efficiency in the results in corrosion inhibition. Its applicability could range from the protection of metal surfaces in corrosive atmospheres to their use for the internal protection of equipment handling acid solutions in the petrochemical industry (Becerra and Gualdron, 2011).

MATERIALS AND METHODS

The weight loss experiments were carried out at room temperature, exposing the films to the different concentrations of hydrochloric acid without agitation, during the time that the test is performed. The carbon steel used was a mild steel with 98% of purity, the sheets had the following dimensions 3×2×0.3 cm.

On the other hand, the LSV tests were carried out in accordance with the norm ASTM G5 (ASTM G102-89, 1999) using a carbon steel wire of 0.7229 mm in diameter as the working electrode.

Extraction of inhibitor: Aqueous extracts were obtained by weighing 20 g of flowers, leaves and stem of *Acmella radicans* without roots then wrapped in filter paper to avoid contamination in the extraction. The filter paper that contains the plant is introduced in the Soxhlet with capacity 250 mL. The 300 mL of distilled water was used as the solvent in a ball flask of 1000 mL of capacity and heating for extraction was allowed to run during 4 h. The assembly of the extraction is shown in Fig. 1. A characterization of the aqueous extracts was carried out, using qualitative and quantitative techniques to know the concentration of the compounds studied.

Weight loss test: Initially, all the steel sheets should be cleaned to remove impurities and dirt, polished with No. 50 emery paper and degreased with acetone. They were then washed with distilled water and dried with filter paper. They were then weighed on a Vibra brand electronic scale (Model HT-220E No. 101880226) to know their weights before being exposed to the corrosive medium (ASTM, 2005).

Each sheet was introduced into a vessel with 40 mL of the hydrochloric acid solutions without agitation and with the different concentrations of inhibitor, this was done for each of the 3 tests and their replicates. Immersion, drying and weighing were carried out for several periods between the first day and the following 15 days. Equation 1 show the corrosion Rate (R) obtained

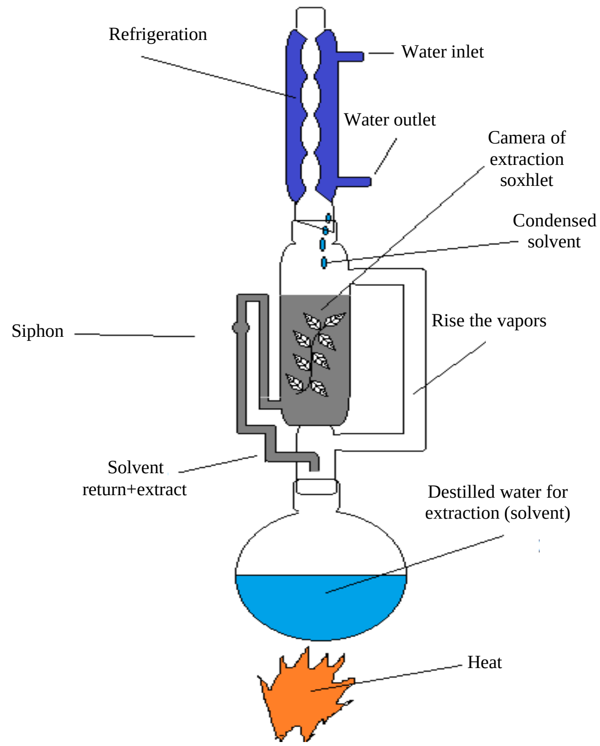

Fig. 1: Experimental assembly for the Soxhlet extraction

by measuring the loss of mass in the first 24 h and converted to millimeters of penetration per year (mmy) according to norm (ASTM G31-72, 2004):

$$R = \frac{K \times W}{D \times A \times T} \quad (1)$$

Where:

K = The 8.76×10^4, dimensionless constant used to get the unit "mmy"
W = The weight losing material in grams (g)
D = The material density, 7.86 (g/cm^3)
A = The area of the material in square centimeters (cm^2)
T = The exposure time of the material to the corrosive environment (h)

Linear Sweep Voltammetry (LSV): The electrochemical measurements were the performed with a typical four-compartment glass cell formed from the carbon steel sample as a working electrode (approximately 0.7229 mm diameter) a Calomel-Saturated Electrode (SCE) as the reference electrode and a rod of platinum (<1 mm in diameter) as a counter electrode and finally a compartment for the entry of nitrogen to keep the cell isolated from any other gas. The reference electrode was connected to a Luggin capillary and the tip of the Luggin capillary was placed very close to the surface of the working electrode

Fig. 2: Mounting of cell for polarization resistance test

to minimize the voltage drop (IR) (Fig. 2). The potentiostat used to control the potential in the electrode cells was a BASS 100 W together with a Faraday C2 box both brand bioanalytical system. In this test we got the corrosion current "icor".

Inhibition efficiency calculation: The efficiency of the inhibitors is defined as the ability to inhibit metal corrosion and is a relationship between the corrosion rate of the metal without inhibitor (white) and the inhibitor. Once the corrosion rates were obtained, the inhibition efficiency (μ) of the *Acmella radicans* extract was calculated using Eq. 2 and 3:

$$\mu(\%) = \frac{R^{*}-R}{R^{*}}\times 100\% \quad (2)$$

$$\mu(\%) = \frac{i^{*}_{cor}-i^{*}_{cor}}{i^{*}_{cor}}\times 100\% \quad (3)$$

Where:

R^* and i_{cor}^* = The corrosion rate and corrosion current without inhibitor

R and i_{cor} = Corresponds to the corrosion rate and corrosion current with *Acmella radicans* inhibitor for the weight loss and electrochemical test, respectively

RESULTS AND DISCUSSION

Collection and characterization of extracts of *Acmella radicans*: The extraction of the extracts of *Acmella radicans* were carried out in aqueous medium using the Soxhlet method to avoid losses of solvent. During extraction by gravimetry, 0.048 g of plant extract was obtained per mL of solution.

Table 1 show the characterization of the aqueous extract which was used for the tests of corrosion by weight loss and electrochemistry can be observed. The tannins are those with the highest concentration 2.82 g/L and substances such as saponins and triterpenes have practically no presence in this extract. Flavonoids and coumarins have a low concentration with respect to tannins 0.94 and 0.06 g/L, respectively.

Electrochemical test: The graphs obtained from the Linear Sweep Voltamperometry (LSV) tests where the tafel polarization curves were obtained are shown in Fig. 3. The corrosion potential is high to the left and the polarization curves present displacement in the logarithm of the corrosion currents towards more negative values in the presence of inhibitor. These displacements are seen in the fact that the polarization curves in the presence of inhibitor are more downstream than in the absence of inhibitor, i.e, they were more negative values. Sastri (2011) explains the relationship between current and resistance to polarization, describing an inversely proportional relation, polarization implies breaking the equilibrium of a reaction by the influence of another, i.e., that the anodic reaction in the metal, theoretically breaks its equilibrium by influence of other reduction reactions.

A smaller corrosion current value in the experiments in the presence of inhibitor with respect to those carried out in the absence of the same (white) indicates a shift towards the initial equilibrium this is reflected in the change in the cathodic branches and anodic in the presence of inhibitor (Fig. 3) indicating inhibition of corrosion by the extracts.

Table 2 indicates electrochemical test result where the efficiency of corrosion inhibition increasing with increasing the inhibitor concentration. Silveira *et al.* (2012) shows that by adding tannins from black acacia tree extracts with a concentration of 2 g/L (*Acacia mearnsii* De Wild) as a corrosion inhibitor in acid medium, found that the anodic branch presented changes towards smaller current densities and this was reflected in the decrease of the corrosion current, reporting inhibition higher than 90%. On the other hand, Rahim *et al.* (2007) found that by adding mangrove tannins (*Rhizophora apiculata*) to a solution of hydrochloric acid, there was variation in the cathodic branch, indicating the decrease in the reduction of H+ to molecular hydrogen and consequently this is reflected in decrease of the corrosion rate with inhibition higher than 80% in acid concentrations between 0.5 and 1 M and tannin concentration of 3 g/L. Amir *et al.* (2014) used coumarins as a corrosion inhibitor, since it has

Table 1: Quantitative characterization in aqueous extract of the *Acmella radicans*

Name plant	*Acmella radicans*		
Metabolite	Concentration (w/v %)	Concentration (g/L)	Method
Cumarins	0.006	0.06	Ultraviolet at 280 nm
Flavonoids	0.094	0.94	Colorimetric with aluminum chloride in methanol at 430 nm
Tannins	0.282	2.82	AOAC 30.184
Saponins	<0.0003	Not representative	Spectrophotometry visible at 528 nm
Triterpenes	<0.00001	Not representative	Liebermann-burchard test

Table 2: Electrochemical test result, corrosion current data for each experiment

Experiment	HCl concentration (M)	Inhibitor concentration (ppm)	Corrosion current i (µA/cm^2)	Efficiency of corrosion inhibition µ (%)
White	1	0	11309	
1	1	2400	9625	14.9
2	1	4800	1921	83.0
3	1	7200	765	93.2

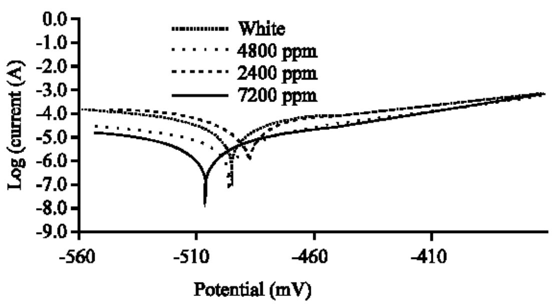

Fig. 3: Tafel polarization curves, potential (milliVolts) versus logarithm of current (Amperes) for carbon steel in different inhibitor concentrations in 1m hydrochloric acid

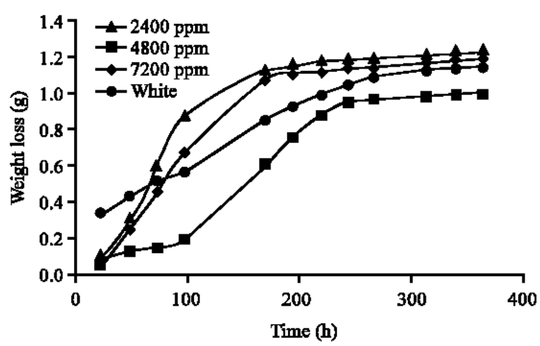

Fig. 4: Variation of weight loss, depending on the time of immersion of carbon steel sheets in hours, presence and absence of extract of *Acmella radicans* in concentration of 1 m hydrochloric acid

sulfur and nitrogen atoms which like the oxygen in the hydroxyl radical can be absorbed into the metal surface and protected.

Weight loss test: In Fig. 4, a noticeable decrease in the rate of corrosion in the presence of the inhibitors can be evidenced before the first 100 h with respect to the targets (inhibitory absence). After this time, until almost 200 h, the curves begin to have the same tendency. This step is due to the formation of a protective metal layer due to the accumulation of oxides on the surface (ASTM G31-72, 2004) and therefore, it is necessary to replace inhibitor from this time.

Table 3 shows as the corrosion rate decreases as the inhibitor concentration increases which is expected as the inhibitory efficiency increases between 60 and 70%. As the inhibitor concentration increases, the abundance of H+ protons causes a more accelerated corrosion which immediately exposes the surface to the action of a more abundant inhibitor which allows a faster migration of the inhibitor to the surface of the metal. On the other hand, Becerra and Gualdron explain that the presence of carbonyl groups allows a stage of protonation by the protons released by the acid. This leads to formation of the hydrates that adhere to the surface of the metal or form complexes with Fe^{+3} in the solution, stopping an important stage for the formation of ferric oxide. This explains why the abundance of more inhibitor. We must remember that hydrates are molecules with free electrons which can form a coordination bond with the surface of the metal (Becerra and Gualdron, 2011).

On the other hand, the behavior evidenced in the graphs of corrosion rate versus time is described by Sastri (2011) who studied the corrosion rate as a function of the concentration of inhibitors, denoting that as the concentration of inhibitor increased decreases the speed of corrosion as well as the efficiency or degree of protection increases.

A higher concentration of inhibitor implies a higher concentration of the components that inhibit corrosion in this case the most representative component were tannins with concentration of 2.83 g/L and its flavonoid monomers. Rahim tested for tannin-based corrosion inhibitors and their monomers (flavonoids) at concentrations of 2-6 g/L from mangrove (*Rhizophora apiculata*) finding inhibition efficiencies above 80% in solutions of hydrochloric acid at 0.5 m and also obtained good results with concentrations of inhibitor of 3 g/L and of acid between 2 and 40 m, describing that the mechanism of protection of the

Table 3: Efficiency result, experiments performed

Parameters	Concentration of ion acid (M)	Inhibitor concentration ion (ppm)	Data obtained test weight loss (g)	Corrosion rate R (mmy)	Average efficiency in corrosion inhibition weight loss test (μ (%))
White	1.0	-	0.37	11.710	-
1	1.0	2400	0.15	4.796	60
2	1.0	4800	0.13	3.924	65
3	1.0	7200	0.11	3.378	70

tannins is through the formation of complexes by the adsorption of these in the surface of the metal or neutralizing the cathode centers (Rahim *et al*., 2007).

It is stated that the corrosion rate decreased in the presence of inhibitor based on *Acmella radicans* effectively, due to the timely appearance of the protective layer due to the adsorption of the anticorrosive substances on the surface of the metal which covered the anode and cathode reaction centers as evidenced in the electrochemical test. Although, the films in the absence of inhibitor also reach the stabilization of the corrosion rate due to deposition of oxides on the surface, this stabilization occurs more slowly than in the presence of inhibitor. In addition, we can say that the tannins played a very important role in the protection of the metal because they were the most abundant phytochemicals analyzed which could be supported by the investigations of other researchers using tannins as inhibitor where they used concentrations of these similar to those of the present investigation, obtaining efficiencies of inhibition above 80% for acid concentrations between 0.4 and 0.7 m.

CONCLUSION

The phytochemical characterization of the extracts of *Acmella radicans* in the aqueous extract through qualitative and quantitative tests, allowed to verify the existence of substances known to inhibit corrosion (saponins, coumarin, flavonoids, triterpenes and tannins). The aqueous extracts showed a significant presence of 3 of these components (coumarins (0.06 g/L) flavonoids (0.94 g/L), tannins with tannins showing highest abundance (2.82 g/L) corrosion inhibitor to the presence of these substances.

The results obtained from the weight loss and electrochemical measurements show that the extracts of *Acmella radicans* are a good corrosion inhibitor in carbon steel in 1 m solutions in HCl, showing inhibitory efficiency of 70% for weight loss method and 93% in the electrochemical test, inhibitor concentrations being effective between 4800 and 7200 ppm. These results are important since they extend the studies on green inhibitors and inhibiting efficiency shown have potential to be applied in the protection of metallic surfaces and the internal care of equipment that operate to acidic conditions in the chemical industry.

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